

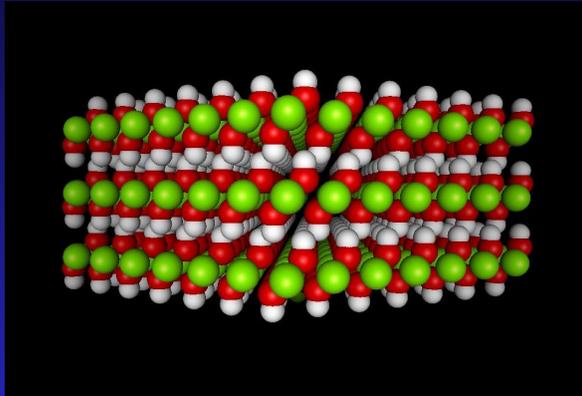
DEVELOPING A MECHANISTIC UNDERSTANDING OF LAMELLAR HYDROXIDE MINERAL CARBONATION REACTION PROCESSES

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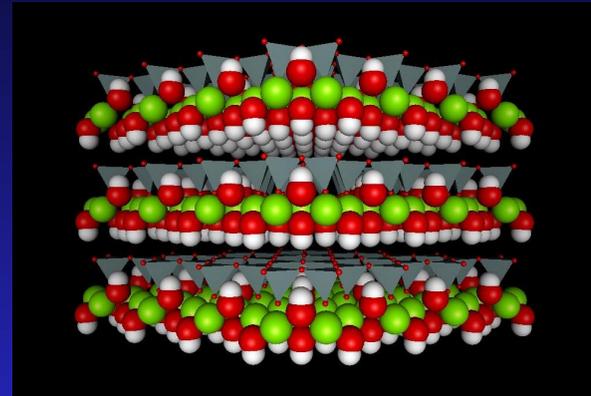
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Mg(OH)₂: A MODEL SYSTEM FOR STUDYING Mg-RICH LAMELLAR HYDROXIDE CARBONATION PROCESSES



Brucite: Mg(OH)₂

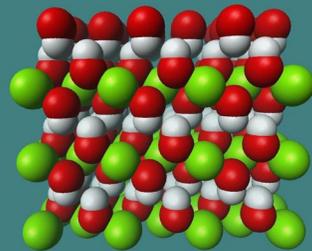


Serpentine (Lizardite): Mg₃Si₂O₅(OH)₄

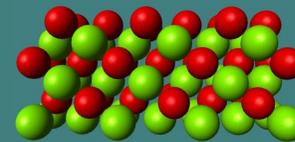
OBJECTIVE: to explore Mg(OH)₂ dehydroxylation/carbonation processes down to the atomic level to identify the key mechanisms that govern carbonation kinetics.

GOAL: to develop an atomic-level understanding of these mechanisms for this model Mg-rich lamellar hydroxide system to facilitate engineering of improved Mg-rich lamellar hydroxide carbonation materials and processes for carbon dioxide disposal.

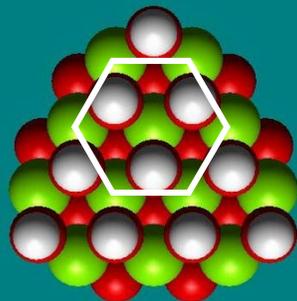
Mg(OH)₂ DEHYDROXYLATION: THE FIRST STEP IN CARBONATION



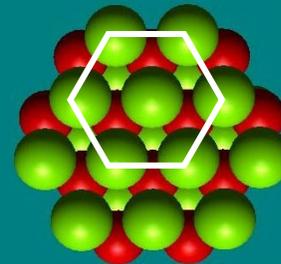
[11 $\bar{2}$ 0] Mg(OH)₂



[10 $\bar{1}$] MgO+H₂O(g)

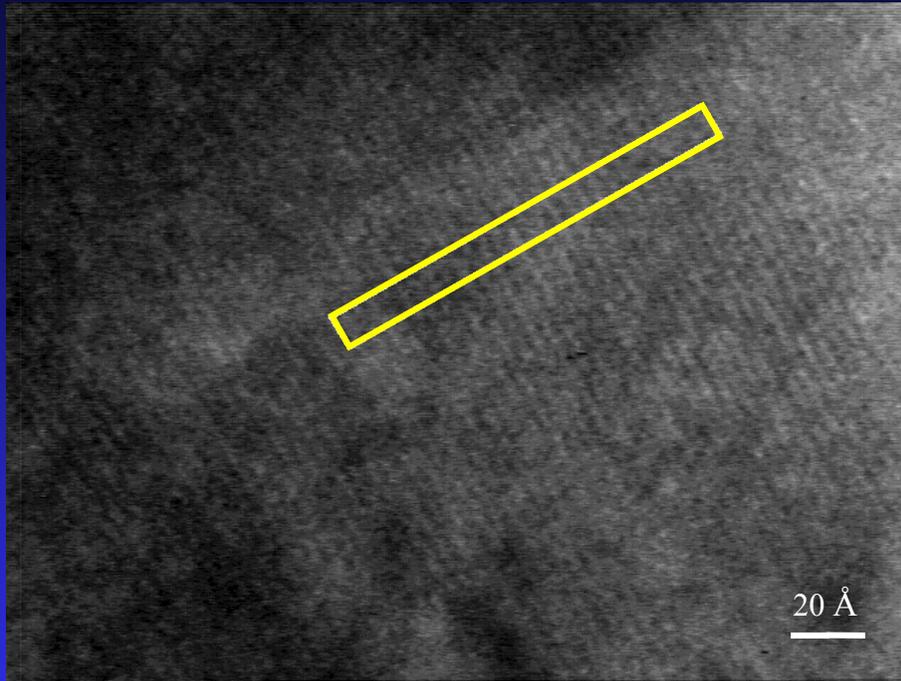


[0001] Mg(OH)₂

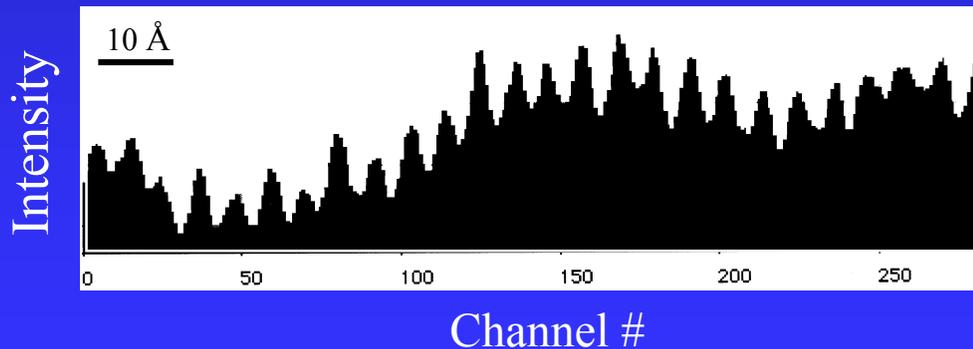


[111] MgO+H₂O(g)

DHRTEM OBSERVATIONS PARALLEL TO THE $\text{Mg}(\text{OH})_2$ LAMELLA PRIOR TO DEHYDROXYLATION

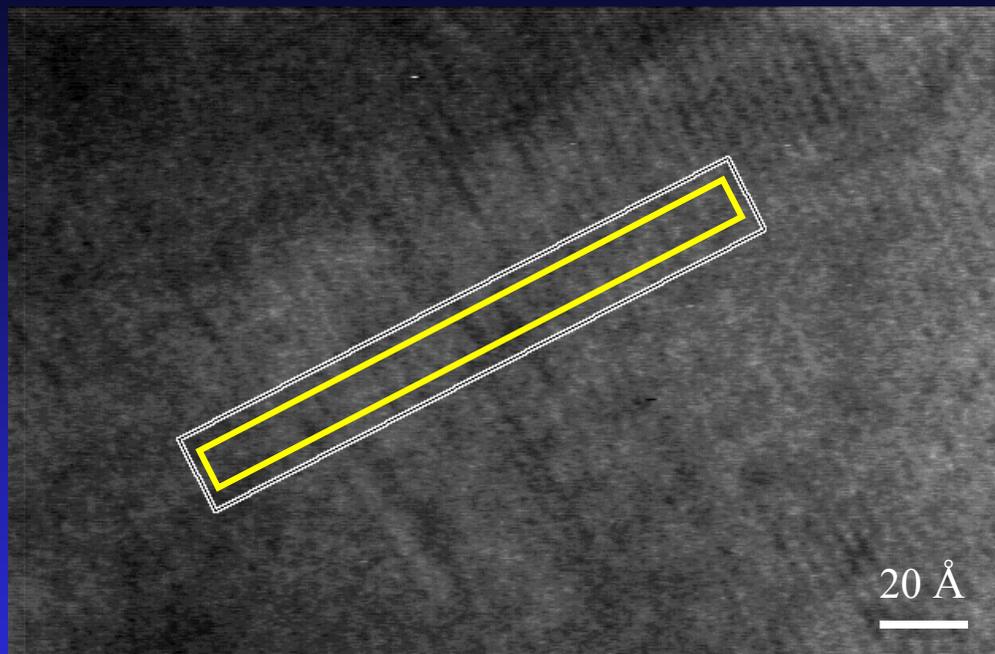


$\text{Mg}(\text{OH})_2$ lamella prior to dehydroxylation as observed using DHRTEM (~ 1 torr H_2O).



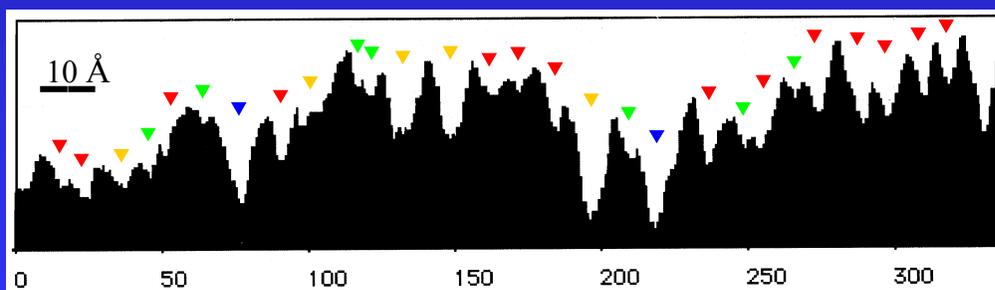
Line profile showing the $\text{Mg}(\text{OH})_2$ interlamellar spacings in the region shown above. All the peak-to-peak spacings measure 4.8 ± 0.5 Å in good agreement with the interlamellar spacing of $\text{Mg}(\text{OH})_2$ determined by XPD (4.769 Å).

DHRTEM OBSERVATIONS PARALLEL TO THE $\text{Mg}(\text{OH})_2$ LAMELLA DURING DEHYDROXYLATION



Behavior of the lamella during dehydroxylation as observed using DHRTEM (~ 1 torr H_2O).

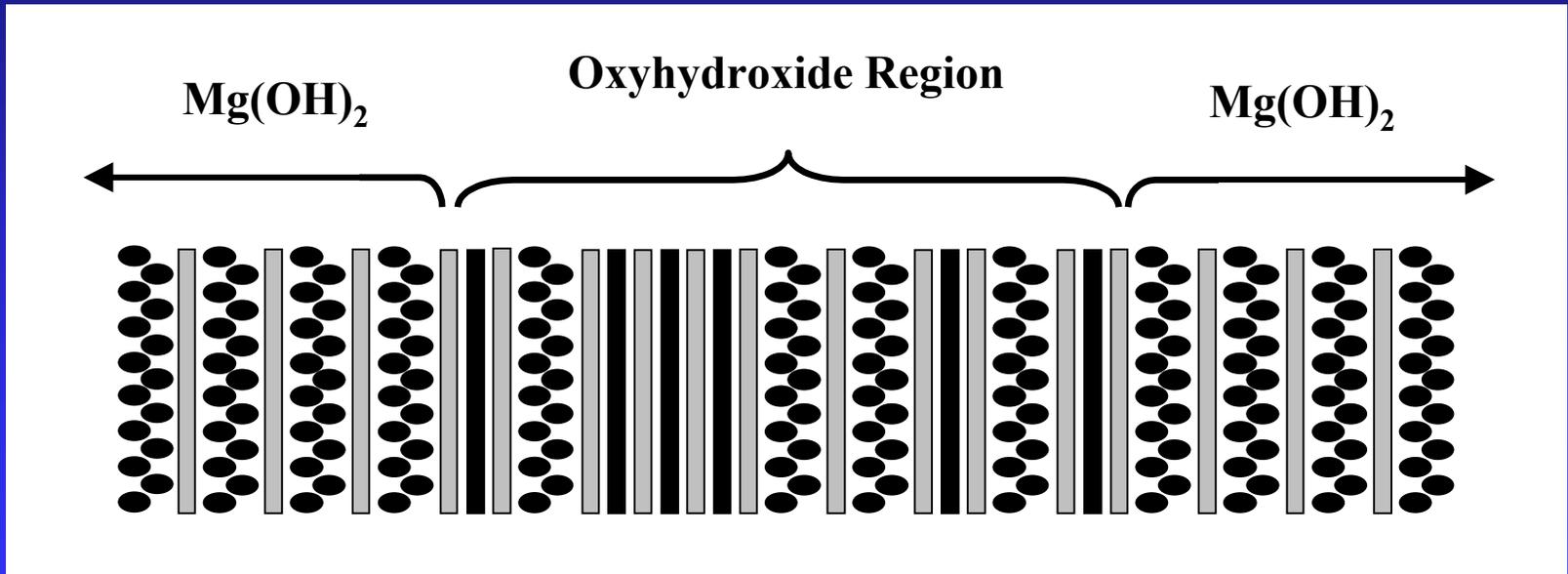
Intensity



Line profile showing oxide, hydroxide, and oxyhydroxide interlamellar spacings in the inner region outlined in the above image. These spacings are in three groups: (i) 2.5 ± 0.4 Å (7 spacings \blacktriangledown ,

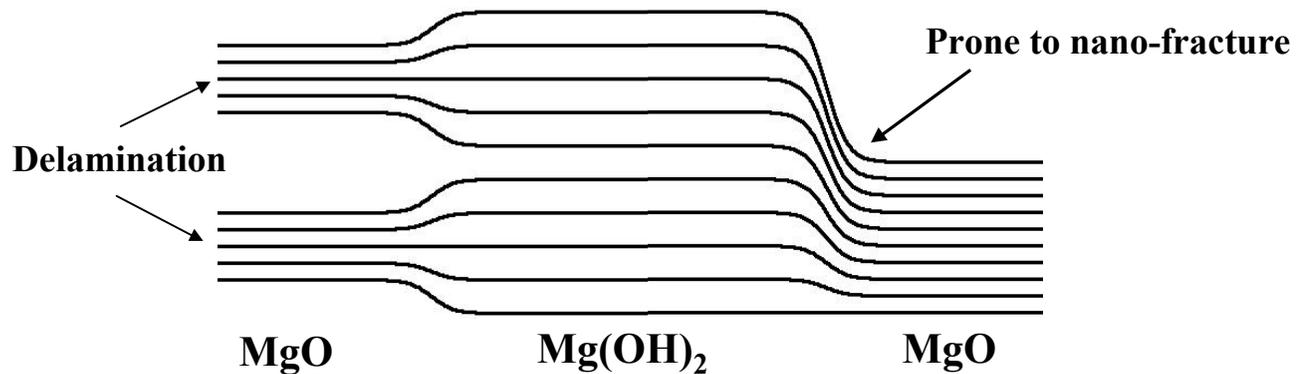
MgO spacing 2.43 Å by XPD), (ii) 4.9 ± 0.5 Å (14 spacings \blacktriangledown , $\text{Mg}(\text{OH})_2$ spacing 4.77 Å by XPD), (iii) 7.3 ± 0.5 Å (5 spacings \blacktriangledown , MgO + $\text{Mg}(\text{OH})_2$ spacing 7.20 Å). Two additional spacings (\blacktriangledown) of 9.0 Å are also observed, which may correspond to $\text{Mg}_3\text{O}_2(\text{OH})_2$ oxyhydroxide lamella (9.6 Å) or dehydroxylating lamella in transition locally.

Mg(OH)₂ DEHYDROXYLATION: INTERMEDIATE OXYHYDROXIDE FORMATION VIA LAMELLAR NUCLEATION AND GROWTH

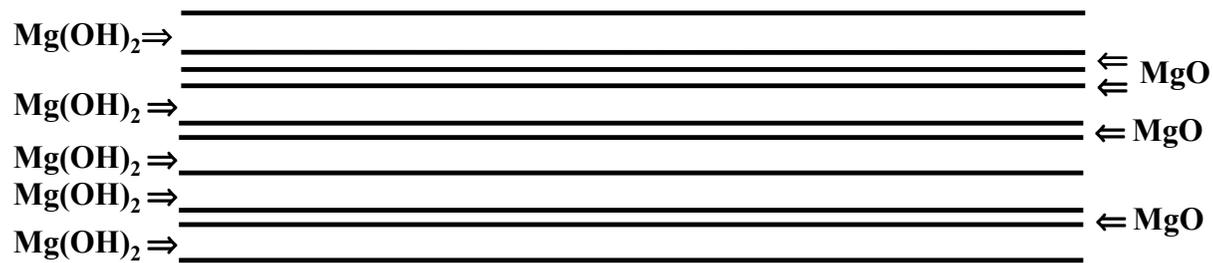


THE EFFECT OF LAMELLAR ELASTIC STRAIN DURING DEHYDROXYLATION

Rapid Nucleation/Slow Growth



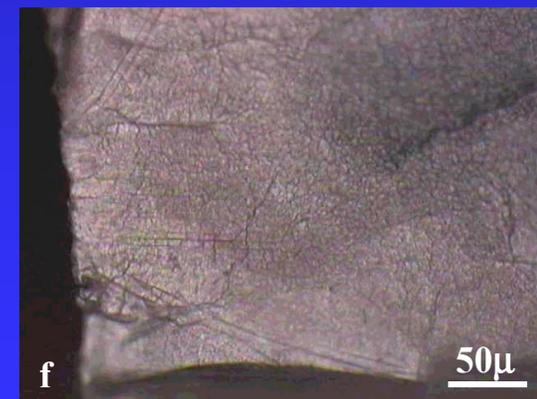
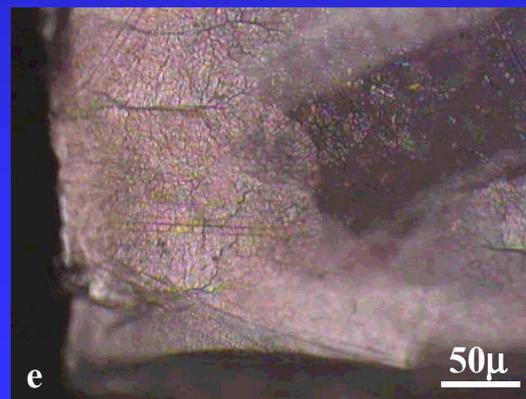
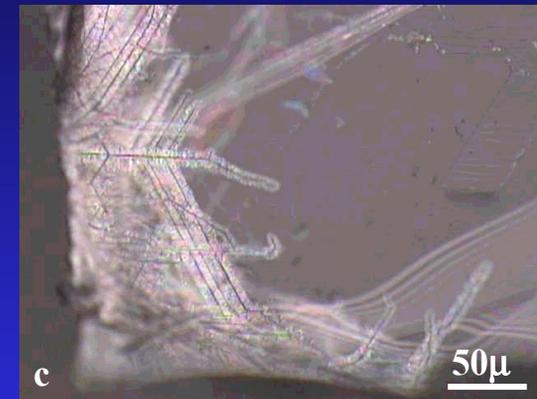
Slow Nucleation/Rapid Growth



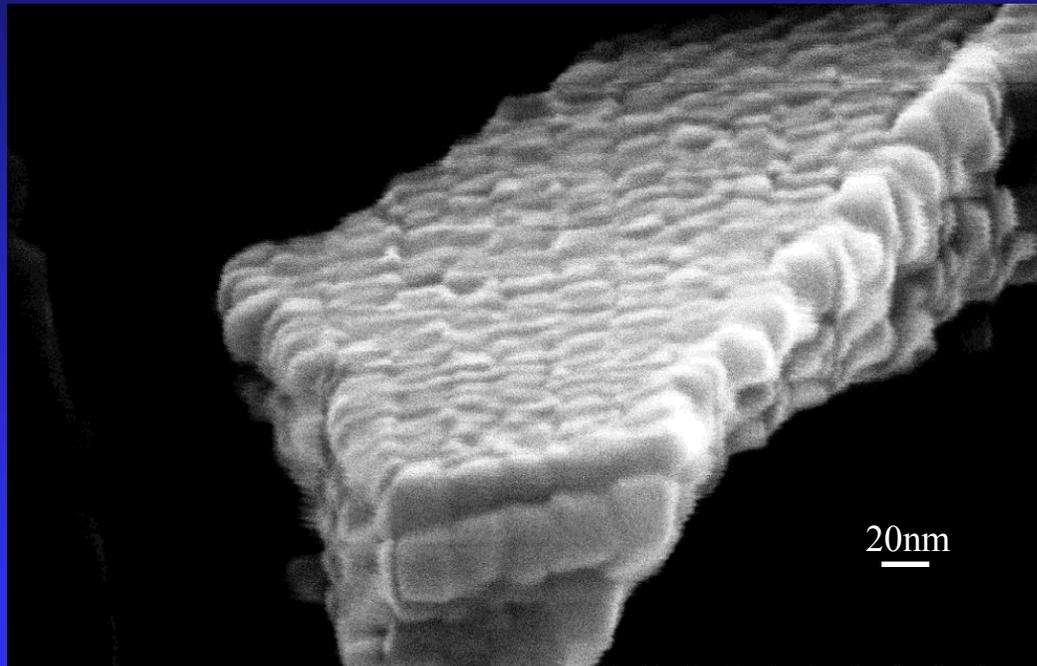
LOW TEMPERATURE DEHYDROXYLATION: OFTEN ASSOCIATED WITH INTERLAMELLAR BLISTER FORMATION



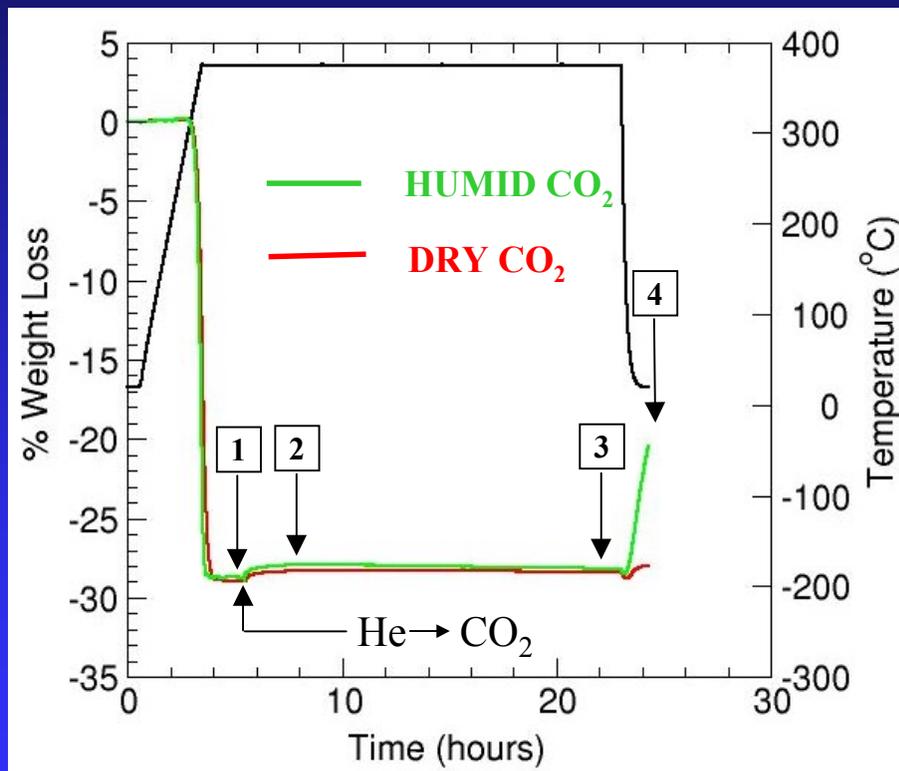
CRYSTAL FRACTURE DURING $\text{Mg}(\text{OH})_2$ DEHYDROXYLATION : ENHANCING REACTION SURFACE AREA



**NANOFRACTURE DURING DEHYDROXYLATION:
LEADING TO MORPHOLOGICAL RECONSTRUCTION
AFTER EXTENSIVE DEHYDROXYLATION AT 580 °C**



CARBONATION OF PARTIALLY DEHYDROXYLATED NANOCRYSTALLINE $Mg_{x+y}O_x(OH)_{2y}$ PSEUDOMORPHS IN HUMID* AND DRY CO_2



HUMID CO_2

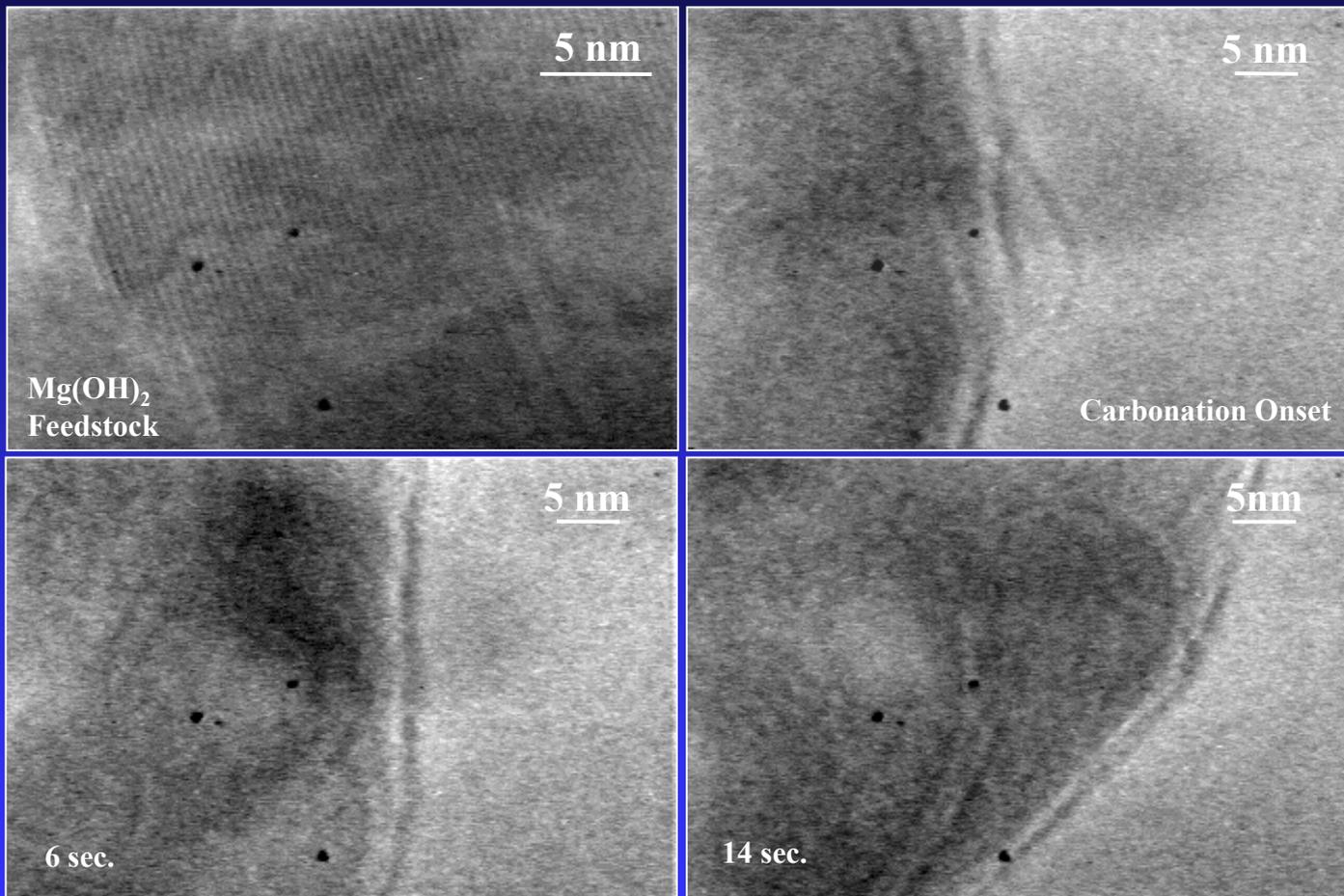
	%MgCO ₃	% MgO	%Mg(OH) ₂
1	0.0	90.2	9.8
2	2.2	88.1	9.7
3	2.2	88.9	8.9
4	14.7	66.2	19.1

DRY CO_2

	%MgCO ₃	% MgO	%Mg(OH) ₂
1	0.0	91.0	9.0
2	1.8	89.2	9.0
3	1.8	89.5	8.7
4	2.7	88.6	8.7

*Humid CO_2 : 1 atm CO_2 + 15 torr H_2O (g)

***IN SITU* DHRTEM OBSERVATION OF AMBIENT TEMPERATURE CARBONATION OF PARTIALLY DEHYDROXYLATED $\text{Mg}(\text{OH})_2$ IN HUMID CO_2 ***

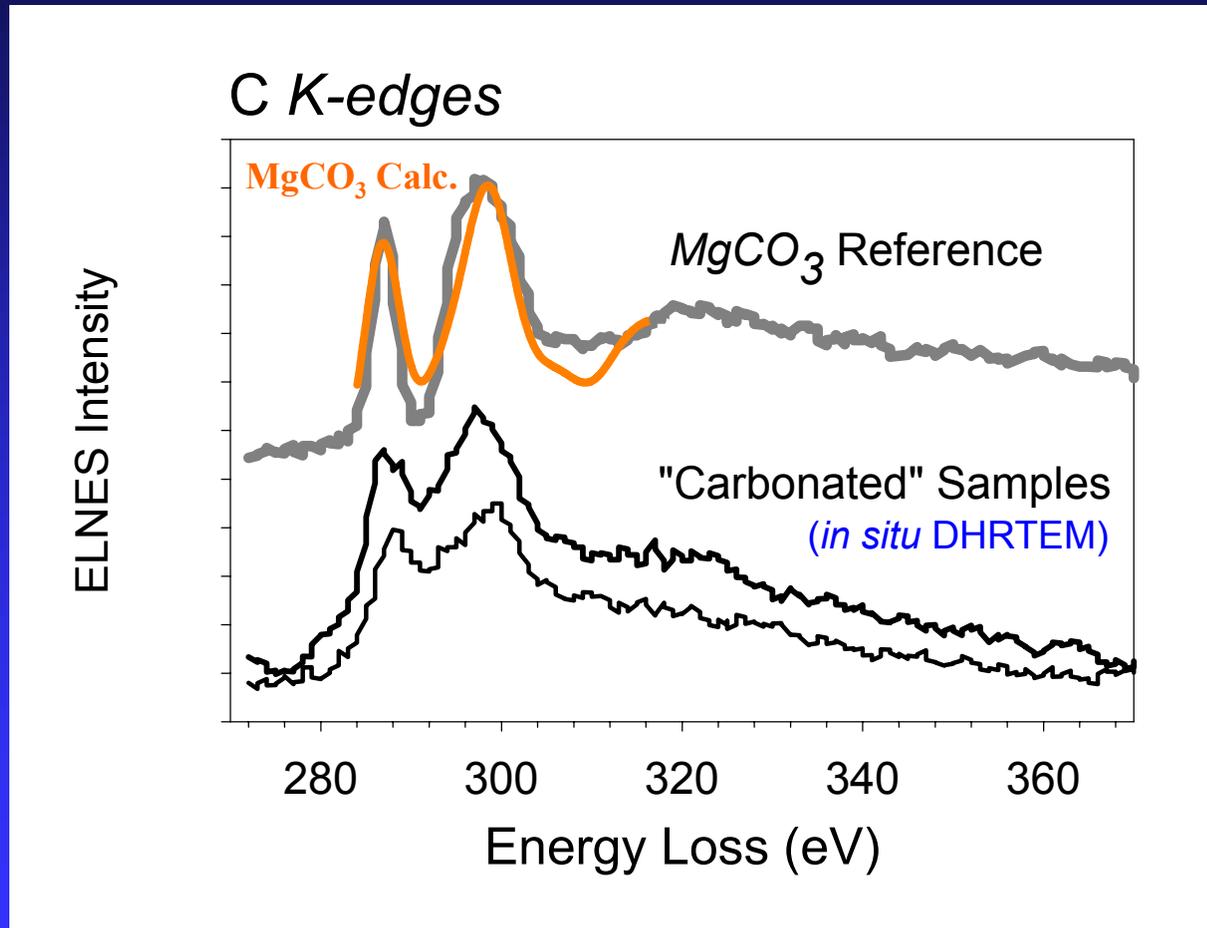


* 400 mtorr CO_2 + H_2O

Carbonation

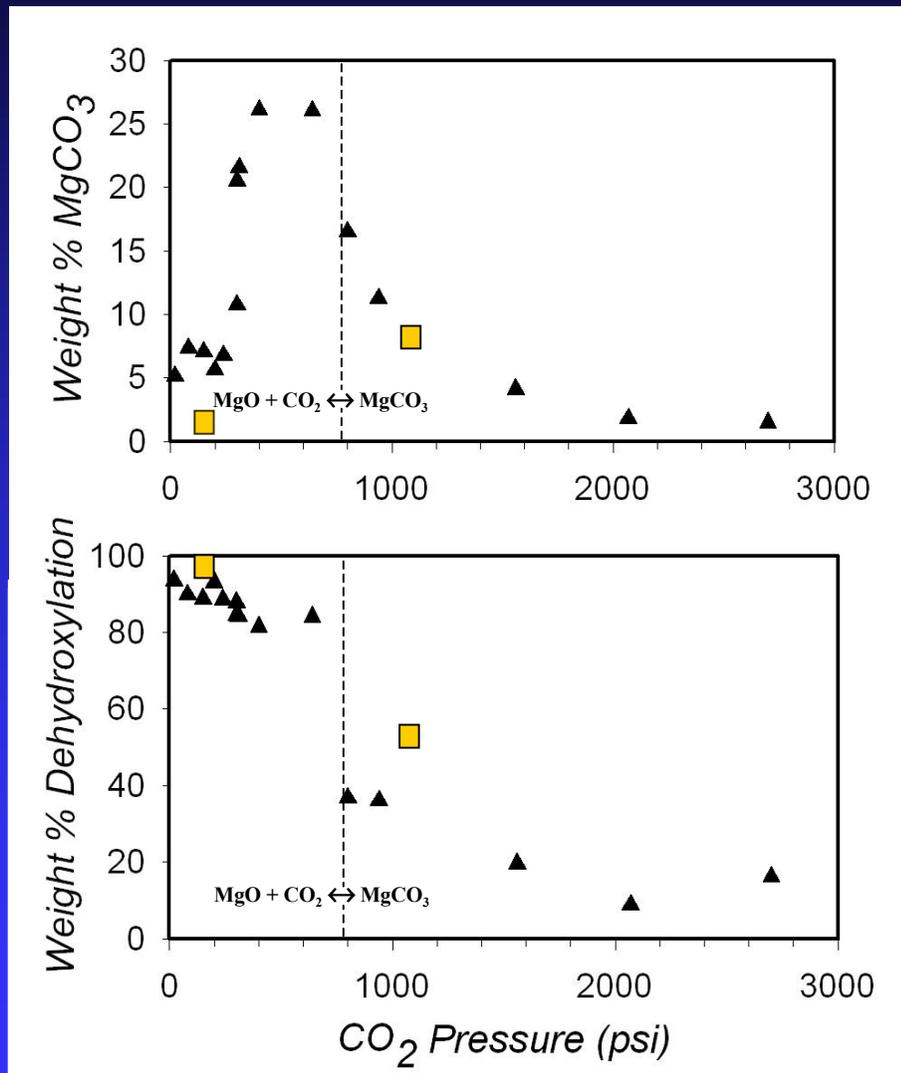
Rehydroxylation

IN SITU PEELS OF AMBIENT TEMPERATURE CARBONATION/REHYDROXYLATION OF PARTIALLY DEHYDROXYLATED $\text{Mg}(\text{OH})_2$ IN HUMID CO_2^*



* 400 mtorr $\text{CO}_2 + \text{H}_2\text{O}$

EXTENT OF CARBONATION AND DEHYDROXYLATION VS. CO₂ PRESSURE*



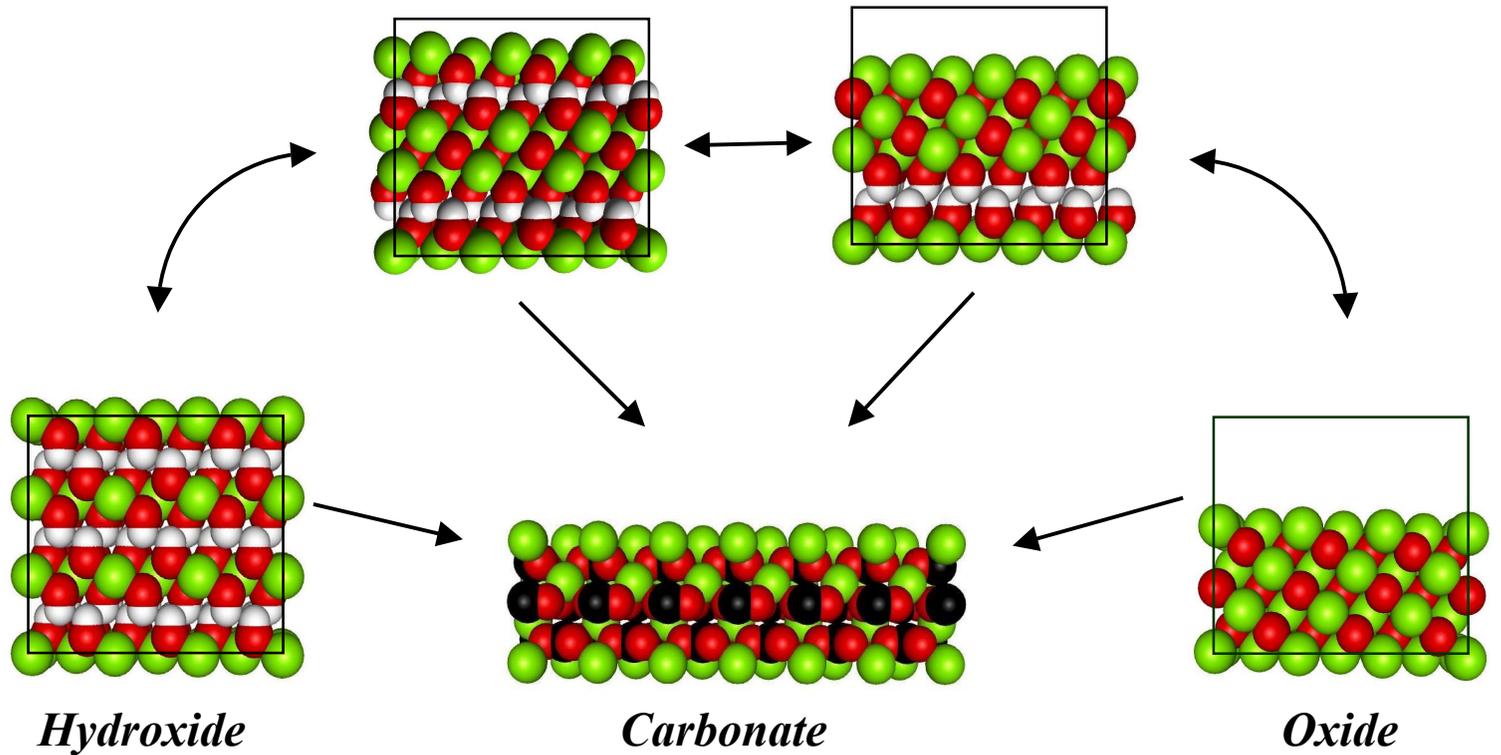
▲ Cooled to ambient temperature under CO₂ (~ 30 min) .

■ Samples quenched from 585 °C and evacuated.

* Samples reacted at 585 °C for 16 hrs.

POSSIBLE CARBONATION REACTION PATHWAYS DURING $\text{Mg}(\text{OH})_2$ DEHYDROXYLATION/REHYDROXYLATION

Intermediate Oxyhydroxide Solid Solution Series

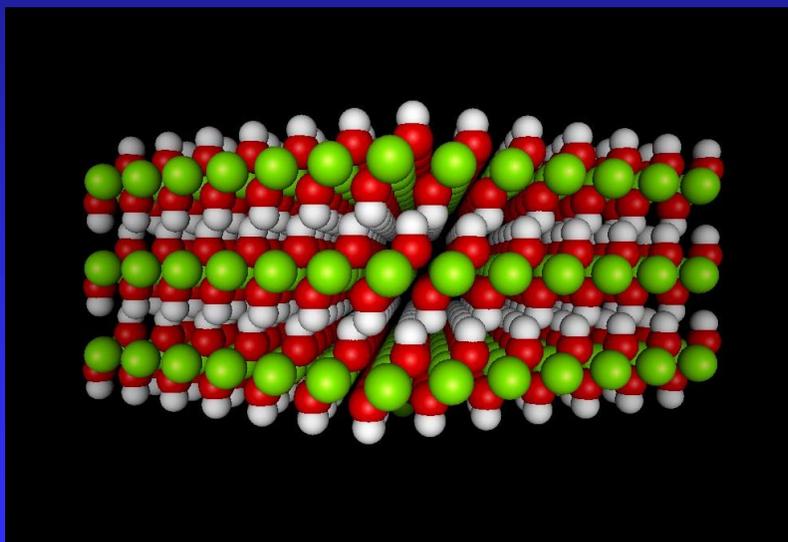


CONCLUSIONS

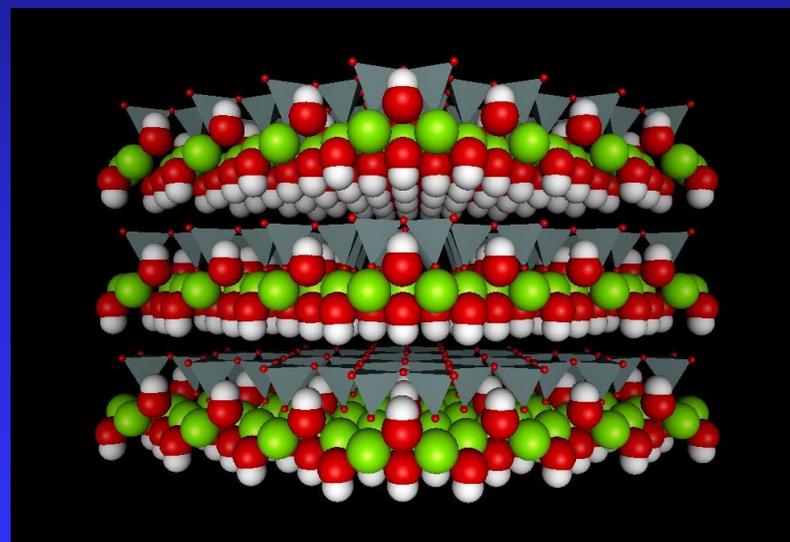
- $\text{Mg}(\text{OH})_2$ dehydroxylation proceeds by lamellar nucleation and growth.
- Elastic stress induced by lamellar nucleation and growth leads to blister formation, delamination, and cracking and surface reconstruction at the nanoscale. These phenomena are key to combating carbonate surface passivation and enhancing carbonation reactivity.
- Carbonation is strongly enhanced by concurrent dehydroxylation or rehydroxylation processes, which can provide access to transitory metastable intermediates (e.g., oxyhydroxides), with higher carbonation reactivity.
- Controlled dehydroxylation/rehydroxylation results in *dramatically enhanced ambient temperature carbonation reactivity* via amorphous carbonate formation.
- Control of lamellar-hydroxide mineral dehydroxylation/rehydroxylation processes offers substantial potential to (i) enhance carbonation reaction rates and (ii) reduce CO_2 mineral sequestration process costs.

EXTENDING THE MECHANISTIC CARBONATION STUDIES OF THE MODEL $\text{Mg}(\text{OH})_2$ SYSTEM TO THE MORE COMPLEX SERPENTINE MATERIALS: LIZARDITE, ANTIGORITE AND CHRYSOTILE

PRELIMINARY RESULTS: THE FIRST FEW MONTHS

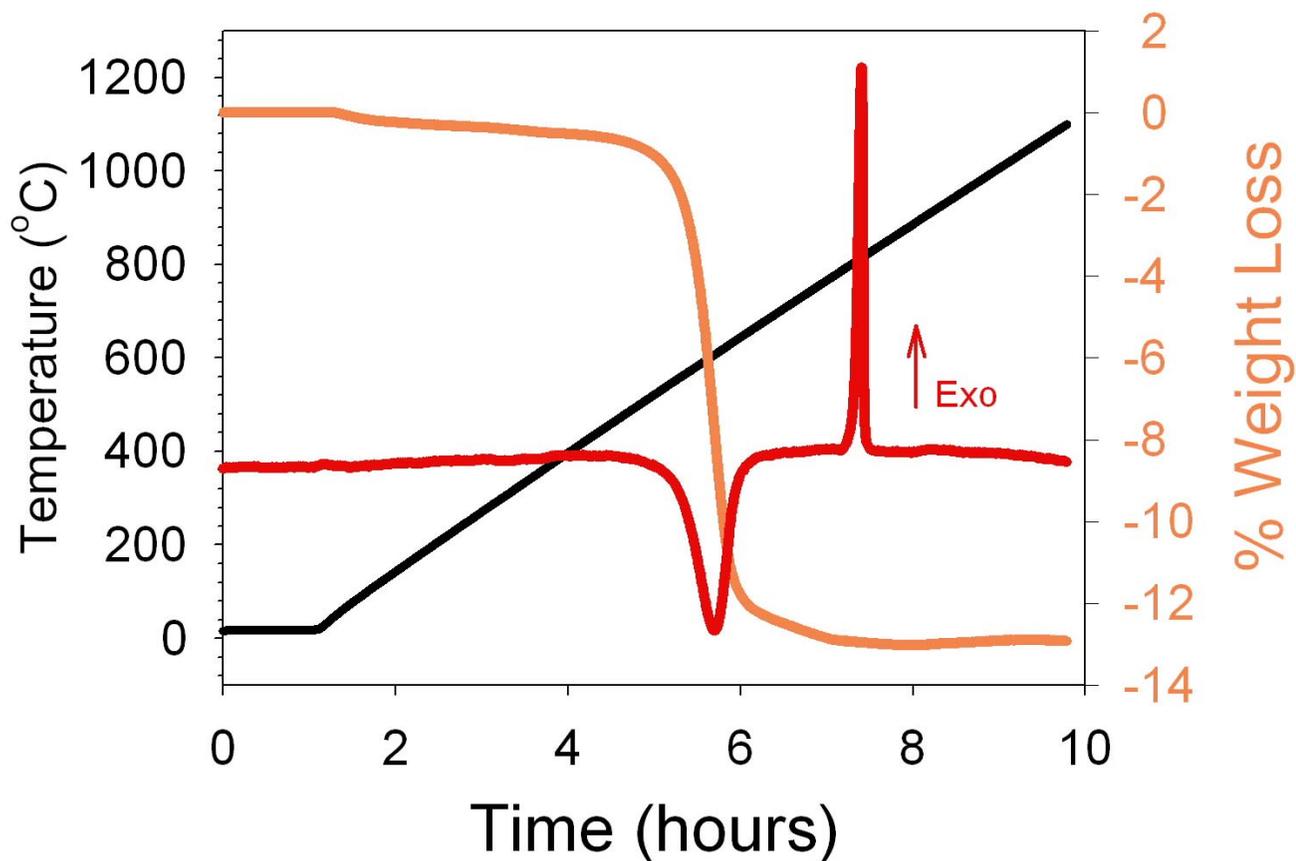


$\text{Mg}(\text{OH})_2$
Brucite

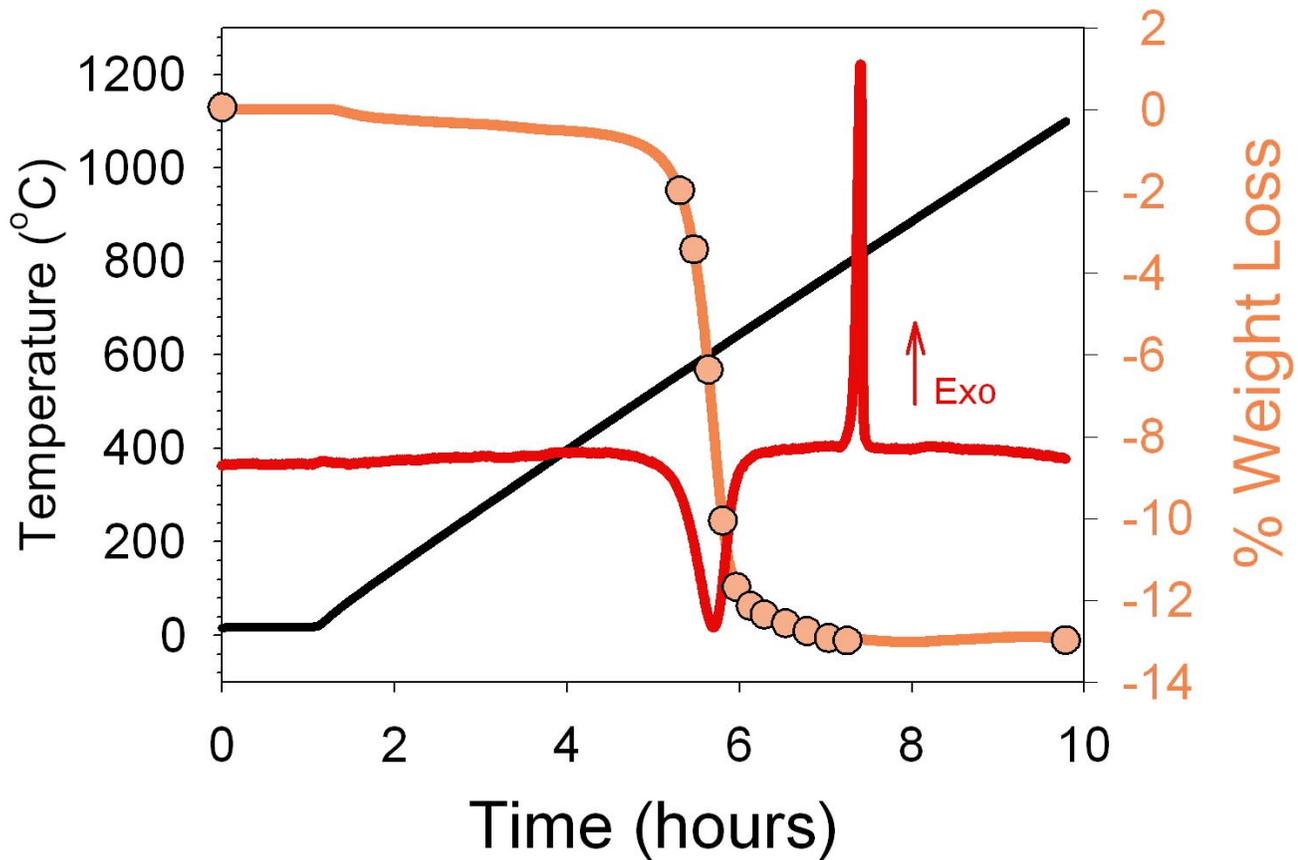


$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$
Serpentine: Lizardite

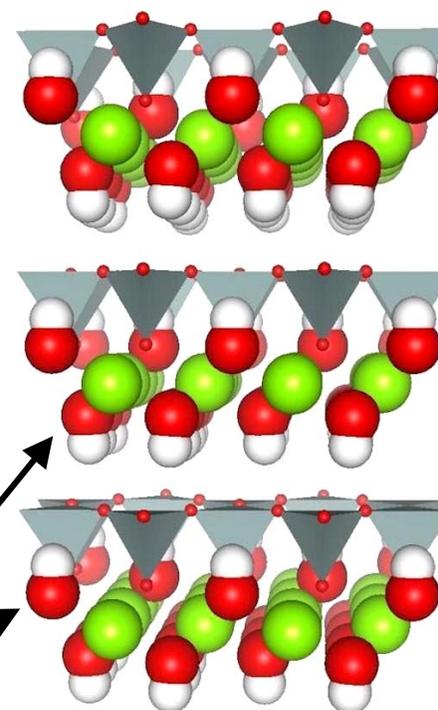
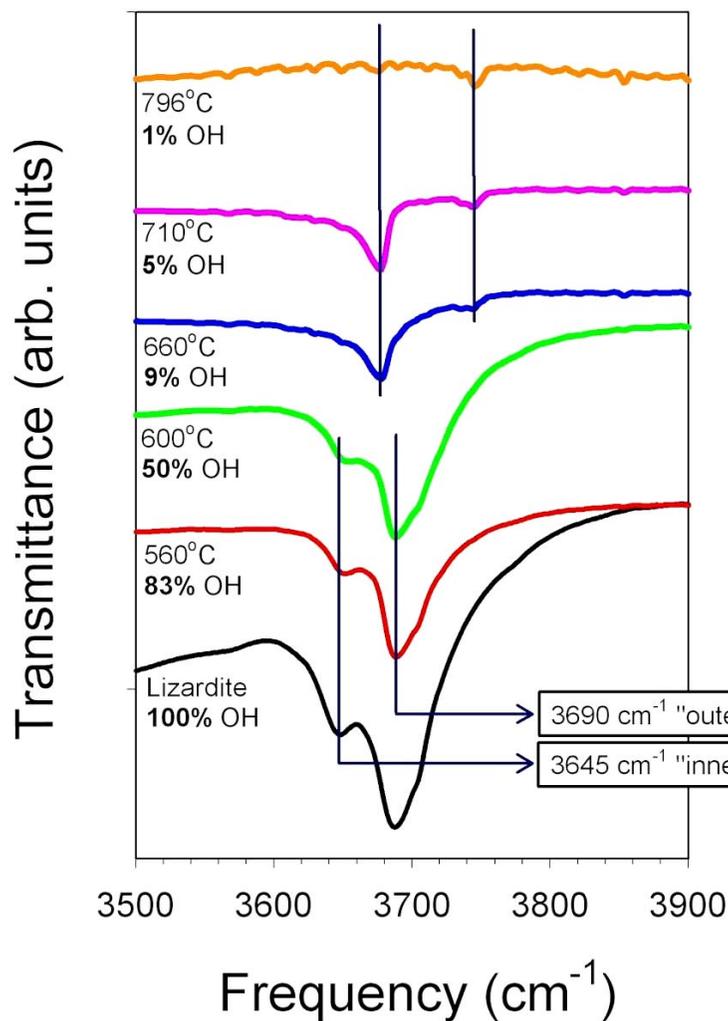
THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS (TGA/DTA) OF GLOBE LIZARDITE UNDER HELIUM



MATERIALS QUENCHED DURING TGA/DTA OF THE GLOBE LIZARDITE HEAT ACTIVATION PROCESS

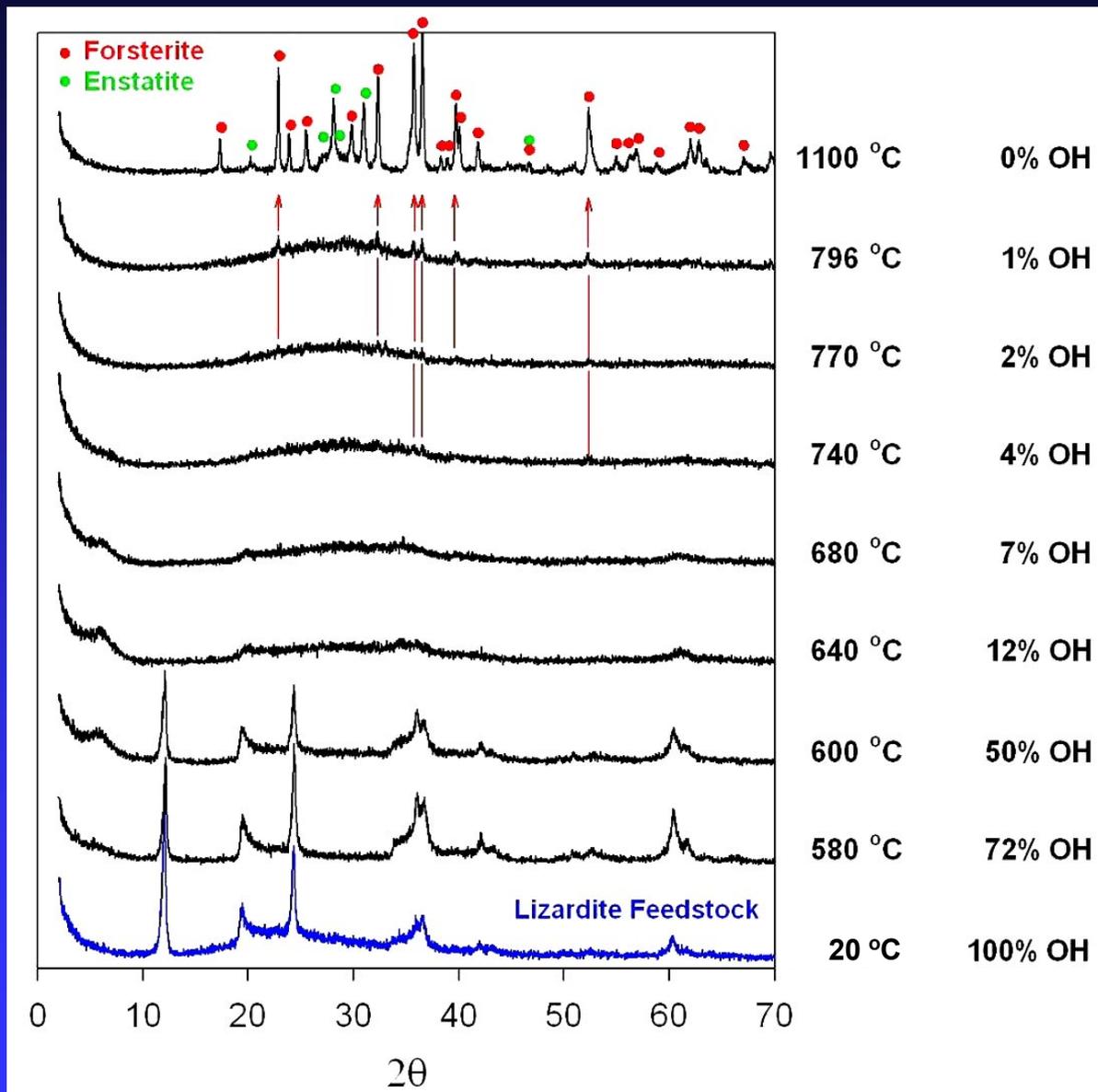


INFRARED ANALYSIS OF HYDROXYL BEHAVIOR DURING LIZARDITE HEAT ACTIVATION

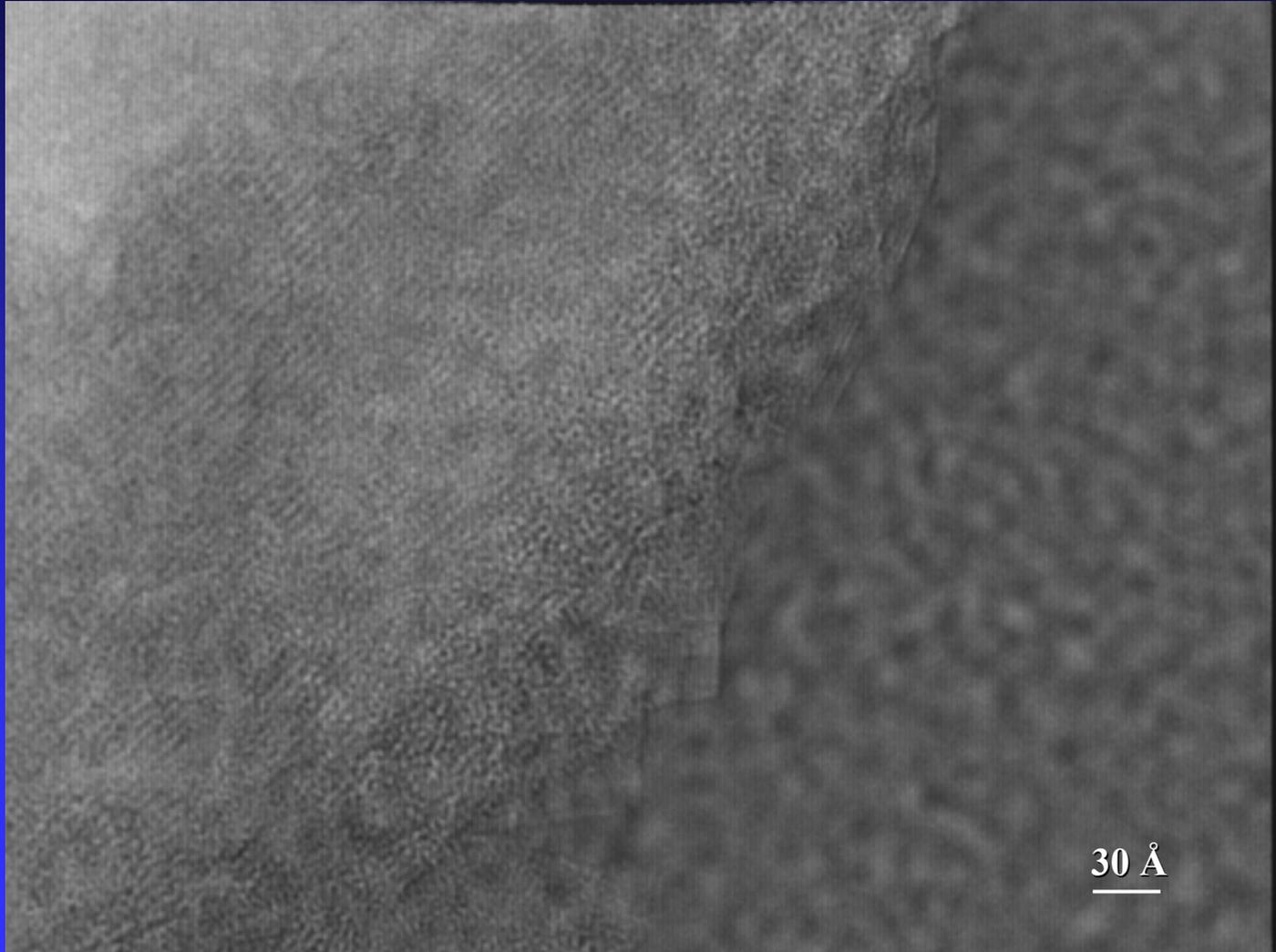


Hydroxyl Diffusion

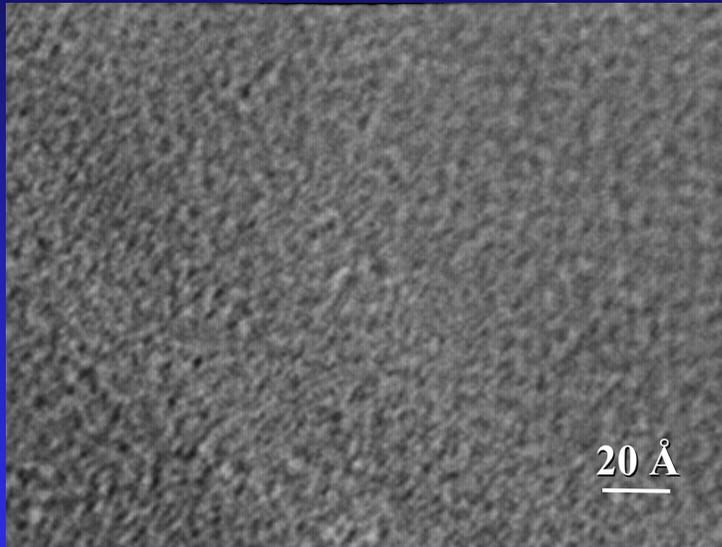
X-RAY POWDER DIFFRACTION ANALYSIS OF LIZARDITE HEAT ACTIVATION



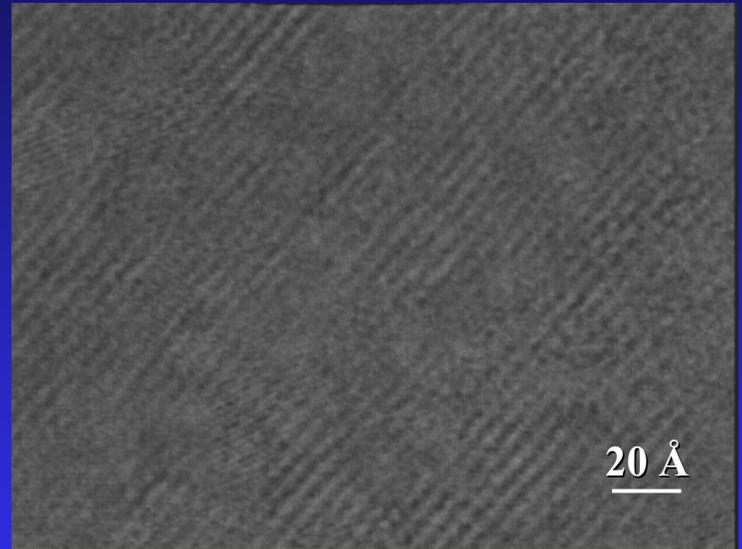
HRTEM OF HEAT-ACTIVATED LIZARDITE QUENCHED FROM 770 °C DURING TGA/DTA



HRTEM OF HEAT-ACTIVATED LIZARDITE QUENCHED FROM 770 °C DURING TGA/DTA



**Amorphous Heat-Activated
Meta-Serpentine Region**



**Region Showing Initial Formation of
5.1 Å Short-Range-Ordered Regions
(indicating forsterite nucleation onset)**

PRELIMINARY CONCLUSIONS

- An unique miniature controlled pressure and temperature reactor is under development to study the aqueous serpentine mineral carbonation process *in situ* using the X-ray synchrotron and Raman facilities at APS/ANL and ASU.
- Heat-activated lizardite (e.g., meta-serpentine) has been isolated at different stages of heat activation for the first time using high purity Globe lizardite.
- The meta-serpentine intermediates formed include a range of amorphous solid-solution and/or locally-ordered material(s) and an intermediate phase with $\sim 15 \text{ \AA}$ interatomic order. These intermediates form and transform on heating, retaining residual OH levels ranging from 12 to 1% after complete lizardite decomposition.
- The OH groups retained in meta-serpentine are contained in an unique structural environment unlike those found in the parent lizardite.
- Heat activation offers substantial potential to control the structure and composition of the meta-serpentine formed during lizardite heat activation.
- Isolation of the most carbonation reactive intermediate(s) should (i) enhance process reaction rates, (ii) lower process cost and (iii) provide a target material to develop lower cost processes to enhance serpentine carbonation reactivity.

FUTURE WORK

- Isolate the most carbonation reactive meta-serpentine intermediate material(s) for lizardite and determine their structure, composition and formation processes.
- Image/analyze their formation process(es) at the atomic level via environmental-cell dynamic high-resolution transmission electron microscopy.
- Extend these studies to antigorite and chrysotile.
- Investigate the mechanisms that govern the aqueous mineral carbonation process via *in situ* X-ray synchrotron and Raman studies of the carbonation process.